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Role of Temperature and Growth Period in the Synthesis of Hydrothermally Grown TiO_2 Nanorods

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Highly uniformed, surfactant free and vertically oriented titanium-di-oxide (TiO_2) nanorods were grown on pre-treated fluorine doped tin oxide (FTO) using hydrothermal method through titanium tetra butoxide ($Ti(OBu)_4$) as titanium source. Three different temperatures 130 °C, 150 °C and 180 °C were followed to grow the nanorods at a fixed reaction time of 4 h. The prepared TiO_2 nanorods were annealed at the temperatures of 550 °C and 600 °C for 3 h. X-ray diffraction (XRD) analysis shows that obtained nanorods exhibit pure rutile phase. From scanning electron microscopy (SEM) analysis, it was found that increasing temperature lead to decreasing the diameter of the nanorods. In addition to these, formation of hierarchical type TiO_2 nanorods were also observed at 130 °C. UV-visible spectra analysis was carried out to find the influence diameter of the nanorods on its optical properties. The plausible mechanism of the growth process was also discussed.

Keywords: Titanium-di-oxide, Solar Cells, Hydrothermal Synthesis, Nanorods, Rutile Phase,

1. INTRODUCTION

Semiconductor nanomaterials based flexible, cost-effective devices fabricated by solution-processed methods is the current area of research interest in order to overcome the future energy crisis. In this regard, synthesis of semiconductor nanomaterials with different dimensions is one of the the most triggered area of research. This is because of the fascinating structural and optical properties of the semiconductor nanomaterials in solution as well as in thin film. Titanium-di-oxide (TiO_2), a wide-bandgap semiconductor ($E_g = 3.2$ eV) is concentrated much for the application of future generation solar cells like dye-sensitized solar cells (DSSCs), quantum-dot sensitized solar cells (QDSSCs) and perovskite solar cells [1, 2]. Hybrid of TiO_2 nanoparticles and semiconducting polymer also analysed for the construction of bulk-heterojunction type of hybrid solar cells in which TiO_2 nanoparticles are effectively functioning as the electron acceptor [3–6]. Moreover, TiO_2 nanomaterials have also proved as potential candidates for the photocatalysis, photoelectrochemical water splitting, sensors and lithium batteries [7–9]. For the solar cell applications, a thin layer of commercially obtained TiO_2 powder (or) sol–gel prepared TiO_2 nanoparticles is deposited on a conducting substrate, typically on a Fluorine doped tin oxide (FTO). A mesoporous structure of TiO_2 is normally used to harvest large amount of photons in DSSC device. Due to the enhanced carrier transport, low recombination rate and high surface area, one dimensional (1D) TiO_2 nanostructures such as nanowires, nanorods (NRs) and nanotubes are considered more beneficial for these kind of applications [10–13]. Therefore, synthesis of 1D TiO_2 nanostructures through simple, cost-effective methods is being preferred. When synthesizing 1D TiO_2 nanostructures using wet chemical methods in presence of long chain capping ligands, removal of these insulating ligands is a tedious process and a programmed post-treatment is often carried out before applying the nanoparticles for the fabrication of potential devices. This is a time-consuming process and also possibility of aggregation in solution is dominated. Thus, surfactant-free synthesis of 1D TiO_2 nanostructures is indeed much useful for the direct application of the fabrication of optoelectronic devices. In the

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synthesis of TiO_2 nanoparticles, sol-gel method based hydrolysis of alkoxide precursor is generally carried out in the presence of strong acid or base [14–17]. Considering the synthesis of TiO_2 NRs, hydrothermal synthesis is the most often used method in order to synthesise the well aligned NRs with optimized dimensions [18–20]. Also, to carry out synthesis through hydrothermal method, very simple precursors and experimental arrangement are required. Among the three phases that exist in TiO_2, rutile phase is exhibiting with improved light scattering properties, high refractive index and very good photocatalytic properties. Thus, synthesis of TiO_2 NRs with rutile phase through hydrothermal method is attracted much in order to utilize it for energy related applications. Apart from the synthesis, the length and diameter of the synthesized NRs could be precisely tuned through controlling the physical parameters such as temperature, reaction time and ratio of the precursors. The first report by Liu and Aydil had opened a pathway in the growth of vertically aligned TiO_2 NRs for solar cells and photocatalytic applications [21]. After this, many experimental efforts were undertaken to grow the TiO_2NRs on a conducting substrate and considerable success was achieved in terms of device efficiency. For instance, Mali et al have achieved over 7% of efficiency using hydrothermally synthesized TiO_2 NRs having dendritic hollow urchin like morphology [22]. Similarly, a three dimensional (3D) hierarchical rutile nanostructures gave an impressive 8.6% efficiency with a metal-free organic sensitizer [23]. In addition to these, further decoration of TiO_2 NRs by other semiconductor nanostructures was found to be enhancing the efficiency still higher [24]. Despite of these experimental results, a clear analysis of influence of physical paramaters on the hydrothermal synthesis of TiO_2 NRs is required. Here, the present work is focussed on the synthesising of TiO_2 NRs with different diameter and length through hydrothermal method at different time intervals. By carefully tuning the physical parameters, we observe that charge-transport of the annealed films would be largely dependent on the morphology change attributed with the synthesized TiO_2 NRs. Critical analysis of influence of temperature on the growth of NRs is much needed in order to explore its role on the crystallinity and charge transport. In this work, the synthesized NRs were annealed at different temperatures and at different time intervals. The structural, optical and morphological changes on the synthesized TiO_2 NRs under the influence of reaction temperature and annealing temperature are addressed in detail.

2. EXPERIMENTAL METHODS

2.1. Materials

Fluorine doped tin oxide, FTO (SnO_2:F), hydrochloric acid (HCl), titanium (IV) butoxide ($Ti(OBu)_4$) obtained from Sigma Aldrich were used for the experiments.

2.2. Synthesis of TiO_2 NRs by hydrothermal method

At first, the FTO coated glass slides were pretreated using acetone and isoproponal for 15 min and rinsed using deionized water to clean the organic residues from the surface. Meanwhile, the precursor solution was prepared using 6M of 90 ml of dil. HCl and 2.5 ml of titanium (IV) butoxide and the mixture was allowed to stirring for 30 min at room temperature. Then, this solution was transferred into a teflon lined autoclave and an FTO coated glass slide was kept inside the autoclave with FTO coated side facing towards downward. The autoclave was sealed tightly and kept in a hot oven for 4 hr. The reaction was carried out at three different temperatures 130 °C, 150 °C, 180 °C respectively. After completion of the reaction, the FTO substrate was rinsed with deionized water and dried under nitrogen air. This substrate was further annealed at different temperatures and different time periods in order to improve its crystallinity and to analyze the role of temperature on the morphology of the synthesized TiO_2 NRs.

Absorption spectra were analyzed using a JASCO UV–visible conventional spectrophotometer in the range of 200–800 nm. SEM images were recorded using the Carl Zeiss MA15/EVO 18 Scanning Electron Microscope. In order to avoid the charging effect, gold/palladium alloy was coated on samples for SEM analysis. XRD patterns were taken using a powder X-ray diffractometer (SEI FERT) JSO DEBYEFLEX 2002 model with CuKα1(λ1/40.154 nm) radiation.

3. RESULTS AND DISCUSSION

The XRD patterns of the as synthesized TiO_2 NRs at different temperatures and annealed TiO_2 NRs at different time periods are given in Figure 1. From the XRD patterns, the 2θ values 26.3, 36.16, 41.2, 54.53, 61.64 are assigned with the (110), (101), (111), (211), and (220) crystal planes of the TiO_2 [25]. All these peaks in the XRD patterns are indicating the presence of tetragonal rutile phase of TiO_2 (JCPDS: 00001-0562). UV-visible spectra analysis of the synthesized TiO_2 NRs at different temperatures is given in Figure 2. In the present work, three different temperatures, 130 °C, 150 °C and 180 °C were selected to carry out the experiment since through literature, we find that the morphology is greatly influenced in these temperatures. To find the influence of annealing time and growth time, the reaction time was kept as 4 h. The UV-Visible spectra show the blue shift in the position of the absorption edge with increasing the temperature. This is because the TiO_2 NRs growth is dependent on the temperature and increasing temperature result much thinner NRs which reflect its absorption. This morphology change is further analysed by the scanning electron microscope (SEM) analysis and the SEM images of the as synthesized NRs at different temperatures are given in Figure 3. The results show that increasing temperature results reduction in the diameter of the TiO_2 NRs due to the changes observed in the growth.

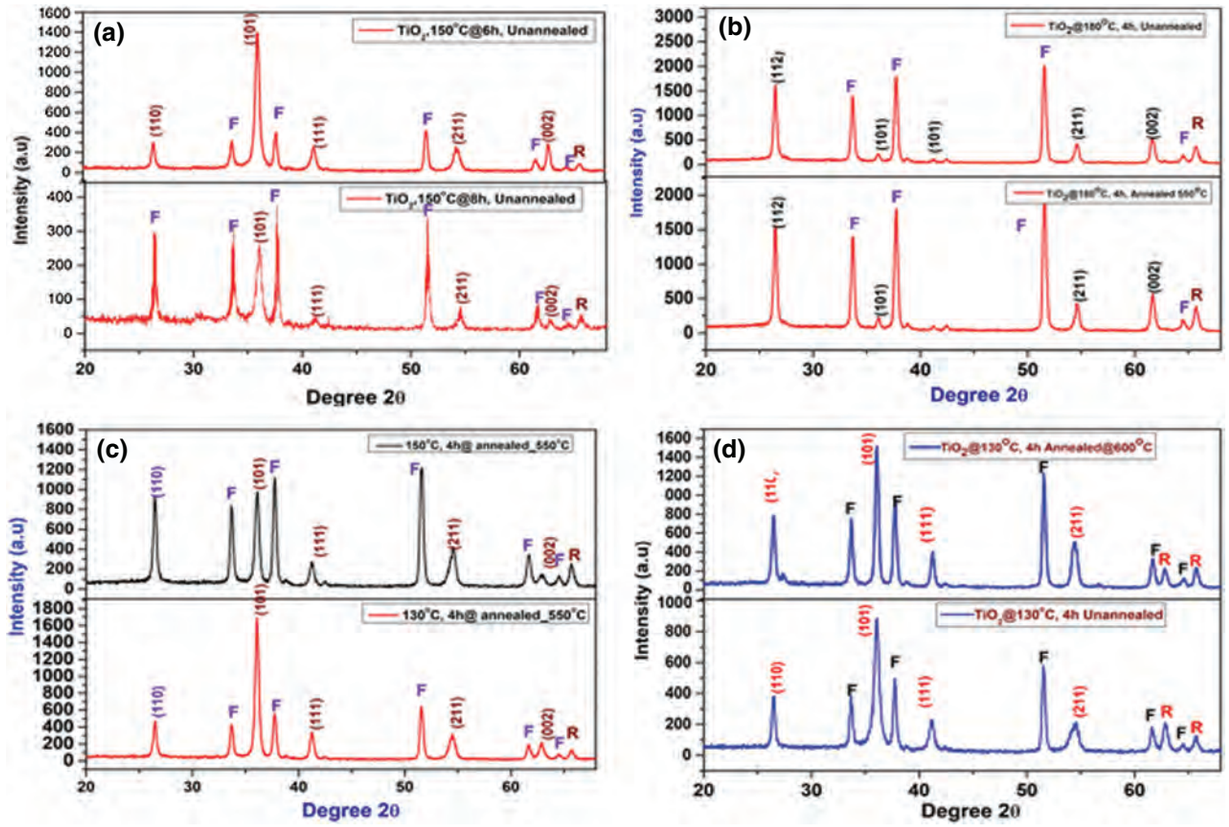

Figure 1. XRD patterns of the (a) Unannelead TiO_2 NRs grown at different reaction periods (b) annealed and unannealed TiO_2 NRs grown at 180 °C (b) different temperatures annealed at 550 °C (c) annealed TiO_2 NRs synthesized at 150 °C and 130°C (d) annealed and unannealed TiO_2 NRs grown at 130 °C (R = rutile, F = FTO).

For the reaction temperature of 130 °C, the formed NRs were possessed with larger diameter compared with NRs formed in other two temperatures (Fig. 3(a, b)). The diameter of the NRs observed in this case were around 130–170 nm. Though the NRs are uniform, it can be seen that the NRs are started to assemble like a cluster in some places. For the growth temperature of 150 °C, the diameter of the synthesized NRs was found to be about 100–120 nm (Figs. 3(c, d)). The cluster assembly behaviour was still higher in this case and this shows that the growth of the NRs can be correlated with the radial growth of the top TiO_2 NRs layer with the bottom layer [26]. For the temperature of 180 °C, it has been found that the shape of the NRs is observed as still thinner one (Fig. 3(e, f)). These observations clearly confirm the significant influence of temperature on the diameter and growth pattern of the synthesized TiO_2 NRs.

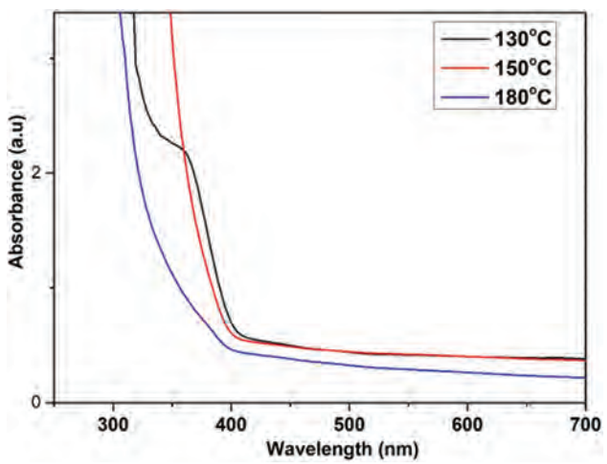

Figure 2. UV-visible spectra of the as-synthesized TiO_2 NRs grown at different temperatures.

The as synthesized TiO_2 NRs were further annealed in order to improve the crystallinity and also to find the role of annealing on the morphology of the NRs. To find the influence of annealing, two different temperatures over 550 °C and 600 °C at two different time periods The SEM images of annealed TiO_2 NRs synthesized at different temperature under different time period is shown in Figure 4.

The results clearly reveal that annealing of TiO_2 at different temperatures improves the crystallinity and also make variation in the diameter of the NRs. For example, when the TiO_2 NRs synthesized at 130 °C are annealed at 550 °C 3 h and 6 h, the diameter of the NRs was

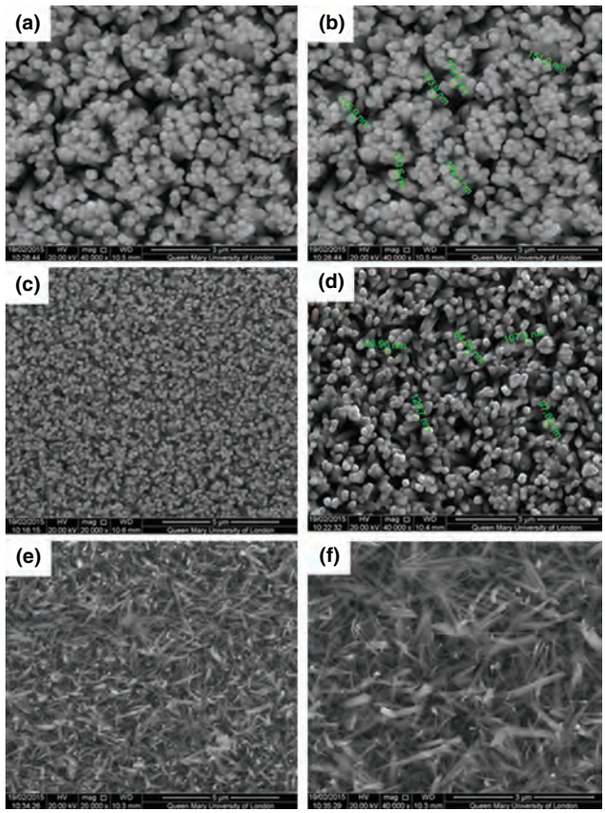

Figure 3. SEM images of the as synthesized TiO_2 NRs at (a, b) 130 °C (c, d) 150 °C and (e, f) 180 °C. The reaction time duration in all these cases was maintained as 4 h.

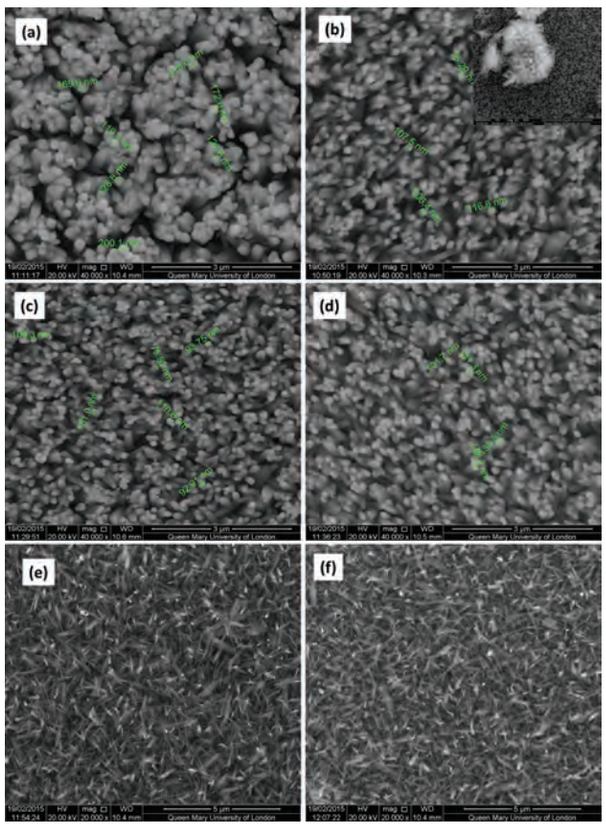

Figure 4. SEM images of the TiO_2 NRs (a) synthesized at 130 °C annealed at 550 °C, 3h (b) synthesized at 130 °C annealed at 600 °C, 3 h and nanoflower morphology of TiO_2 NRs (inset) (c) synthesized at 150 °C annealed at 550 °C, 3h (d) synthesized at 150 °C annealed at 600 °C, 3h (e) synthesized at 180 °C annealed at 550°C, 3 h (f) synthesized at 180 °C annealed at 600 °C, 3 h.

reduced from 120–200 nm to 75–120 nm (Fig 4(a, b)). Furthermore, it was found that formation of nanoflower like morphology was observed in the TiO_2 NRs annealed at 550 °C for 3 h. Formation of nanoflower morphology of TiO_2 NRs under the influence of foreign ion, ionic liquids are already observed [27, 28]. In the present case, it is due to the increasing the annealing temperature and hence the significance of annealing in the formation of NRs through tuning the physical parameters has to be analysed in detail. Similarly, variations in the diameter was also observed for the 150 °C synthesized TiO_2 NRs annealed at different temperatures (Fig 4(c, d)). For the NRs synthesized at 180 °C, extremely thin shaped NRs were observed for the NRs annealed at 3 h and 6 h (Fig. 4(e, f)). It was also observed that these NRs are entirely different from the pristine TiO_2 NRs synthesized at different temperatures. The schematic diagram of the change of morphology of the NRs at different temperatures is given in Figure 5. The clear mechanism of the formation of TiO_2 NRs is described as follows. At initial stage, the alkoxide precursor (TBT) provide an atmosphere to generate the rutile nuclei on the surface of the substrate (FTO). During the reaction progress, the Ti^{3+} from TBT getting hydrolysed and formation of $TiOH^{2+}$ takes place in solution. Because of the dissolved oxygen present in the water, this $TiOH^{2+}$ is oxidised and formation of Ti (IV) takes place. Through this Ti(IV) as the seed, growth of TiO_2 NRs takes place in the solution. This formation of TiO_2 initiated with the formation of TiO_6 octahedra network and the growth of this octahedra network leading to extended chain like structure. Since growth of this structure takes place through [001] direction and through lowest surface energy plane {110}, formation of rutile structure is more favoured. Finally, a well oriented NRs array was obtained through the continuous supply of Ti(IV) nuclei from the solution. The presence of HCl prevents the continuous hydrolysis of the precursors and also encourage the growth

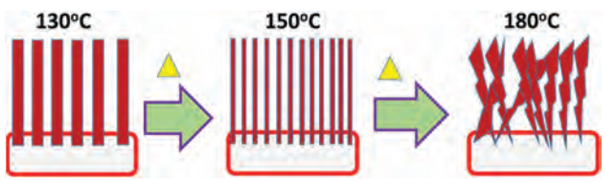

Figure 5. Schematic diagram of the formation of TiO_2 NRs with different dimensions at different reaction temperatures.

of NRs at [001] direction [9]. This significant influence of HCl on the growth of the TiO_2 NRs also confirmed in previous observations [29–31]. Here, we followed three different temperatures 130 °C, 150 °C and 180 °C. At the lower temperature ie, 130 °C, the building block of the growth of TiO_2 NRs is not disturbed by the temperature and growth facilitates without any disturbance. However, the individual NRs are not isolated in this case due to the growth pattern and when we annealed this film at higher temperature, because of this clustered growth, hierarchical nanoflower like structure was observed. This also continues at the temperature 150 °C. However, compared with 130 °C, the NRs grown at 150 °C are possessed less diameter but well isolated growth pattern of individual NRs. As the temperature continues, at higher temperatures, for example 180 °C, because of the accelerated growth, the resultant NRs are appeared as the sheet like structures. It was observed in the present case the NRs formation takes place only when equal volume of water is used with the equal volume of the HCl. Modulation of volume in both cases resulted absence of NRs formation on the substrate (FTO) which clearly represents the importance of volume of reactants on the growth of the NRs.

4. CONCLUSIONS

Synthesis of TiO_2 NRs by hydrothermal method at different temperatures result NRs with different morphologies due to the influence of growth pattern with respect to temperatures. Synthesis of TiO_2 NRs using hydrothermal method provide a versatile approach to regulate the diameter as well as dimensions of the NRs. Further effort in utilizing these tunable nanostructures for photochemical conversion, photo catalysis applications through heteronanostructure configuration will lead a new avenue in terms of efficiency. Also, the carrier transport analysis of these structure will open other possible ways to explore their potential utilization for future devices.

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